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"CHARACTERIZATION OF CELLULOSE AND POLYPEPTIDE POLYMERS"

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Introduction and Summary

"EXTENSION OF THE THEORY OF LIGHT SCATTERING FROM POLYMER SOLUTIONS"

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INTRODUCTION AND SUMMARY

In order to use the experimental data obtained by studying the angular distribution of the light scattered by a macromolecular solution, it is necessary to compare the experimental results with theoretical results derived for various models of the macromolecules. Until now, almost all the study on molecules have been based on Debye's calculation of the scattering factor $P(\theta) = \frac{I(\theta)}{I(0)}$ when $I(\theta)$ is the intensity scattered for an angle θ between incident and scattered beam which gives

$$P(\theta) = \frac{2}{u^2}\left[1 - u + \exp(-u)\right] \qquad \text{with}$$

$u = \left(\frac{4\pi}{\lambda'}\sin\frac{\theta}{2}\right)^2 \frac{b^2N}{6}$, λ' the wave length of the light in solution, b the effective bond length of the chain, and N the degree of polymerization.

This formula is based on the assumption that N is very large and that the distances between every pair of elements have a Gaussian distribution. In the following we consider: first, an alternative to the assumption just mentioned; second, the effects of branching of the polymer molecule and the polydispersity of the polymer sample on the scattering factor; and third, a precise treatment of the depolarization light scattered from chain molecules which offers the possibility of characterizing the molecules when N is so small that the particle scattering factor is unity with the

consequence that information cannot be obtained from angular intensity measurements.

I. In many problems concerning the statistics of chain molecules, one replaces the chain by a spherically symmetrical distribution of points around the center of mass. Isihara and Debye have evaluated the density distribution function w(r) for this case and we have used it for the evaluation of $P(\Theta)$ as shown in Part I. The results show that this assumption leads to a markedly different $P(\Theta)$ and for practical purposes should not be used. The difference in $P(\Theta)$ for the two different density distributions contrasts with the fact that they lead to similar results in other problems, such as the calculation of intrinsic viscosity. This is due to the fact that the contribution of a pair of elements is important in light scattering when these elements are far apart while in hydrodynamic problems it is the contrary.

II. It is well known that branching and polydispersity are the two most important properties of polymers that cannot be readily estimated. Since both of these affect $P(\Theta)$, we have tried to find out what definite information about these points can be obtained from light scattering.

Zimm has already evaluated the effect of polydispersity on $P(\Theta)$ for a certain kind of distribution and Zimm and Stockmayer have given the first term of the expansion of $P(\Theta)$ when branching is present. Since, when $P^{-1}(\Theta)$ is plotted as function of $\sin^2 \frac{\Theta}{2}$, the curve usually has a very small curvature, the asymptotic behavior of these curves can be obtained experimentally for sufficiently high molecular weight. We have been able to derive two simple relations characterizing the branching and polydispersity by comparing the initial slope to the slope of the asymptote, and to show that, in the case of polydispersity,

the determination of $P(\theta)$ over the whole range gives $\langle M_n \rangle$, $\langle M_w \rangle$, and $\langle M_z \rangle$ in addition to the dimension.

III. Angular intensity data from polymer solutions are usually interpreted neglecting the depolarization of the scattered light. This approximation is quite good for long chains but in the case of short chains the depolarization can be an important correction and its study can be interesting in itself.

In Part 3 we have derived an expression for the anisotropy of a chain molecule as a function of the anisotropy of the monomeric unit and of the valence angle. The results show a simple relation between the anisotropy and the root-mean-square of the end-to-end distance. This is particularly useful since if the chains are short we cannot determine their end-to-end distance by the usual light scattering methods. In this case the study of the anisotropy should provide us with this kind of information.

The set of formulas we have established in this case can also be used for studying the effect of the interactions of the anisotropy of a fluid. We plan to study this effect in the future, and we give here only a general formula for the evaluation of the anisotropy.